

(12) UK Patent Application (19) GB (11) 2 247 461 (13) A

(43) Date of A publication 04.03.1992

<p>(21) Application No 9117869.9</p> <p>(22) Date of filing 19.08.1991</p> <p>(30) Priority data (31) 02227800 (32) 29.08.1990 (33) JP 02229828 30.08.1990</p>	<p>(51) INT CL<sup>5</sup> C08L 83/10, C09D 183/10</p> <p>(52) UK CL (Edition K) C3T T201 T226 T321 T333 T361 T363 T364 T505 T507 T509 T522 T524 T563 T601 C3M MFNY M103C M120C M123C M201 U1S S1391</p> <p>(56) Documents cited GB 2012786 A EP 0114512 A EP 0098940 A JP 61078806 A JP 01069673 A US 4093673 A</p> <p>(58) Field of search UK CL (Edition K) C3T INT CL<sup>5</sup> C08L 83/10, C09D 183/10 Online databases: WPI; CAS-ONLINE</p>
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(54) Polysiloxane and resin coating composition

(57) The invention provides a heat-curable resin composition comprising (I) a polysiloxane resin prepared by condensation of a silane compound having at least one hydroxyl group and/or hydrolyzable group respectively directly attached to the silicon atom, and (II) a hydroxyl-containing resin or a hydroxyl- and carboxyl-containing resin.

The polysiloxane is preferably prepared from tri-alkoxysilanes and may additionally contain an epoxy substituted hydrocarbyl group. The resin (II) is conventional.

The composition is used for coating substrates and has good storage stability and gives a gloss finish.

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## CURABLE RESIN COMPOSITION AND CURING METHOD

The present invention relates to a novel curable resin composition and a method of curing the same.

5 Numerous curable compositions containing hydroxyl groups and alkoxy silane groups as functional group components have been heretofore proposed. Of the proposed curable compositions, however, none are satisfactory for use. For example, a mixture of a hydroxyl-containing resin and a copolymer containing an alkoxy silane vinyl monomer as  
10 an essential monomer component is known. Yet the mixture is unsatisfactory in that it has a low storage stability and can not give a glossy cured coating because of the shrinkage formed in the surface of the coating due to the difference in the curing rate between the surface and the interior.

15 Also known is a curable composition comprising a polycarboxylic acid resin and a polyepoxy compound. The composition necessitates baking at a high temperature of 160°C or higher for a low reactivity between the carboxyl group and epoxy group, disadvantageously entailing a high  
20 production cost.

It is an object of the present invention to provide a novel curable resin composition free of the foregoing drawbacks and a method of curing the same.

It is another object of the invention to provide a

novel curable resin composition which is excellent in storage stability and curable at a relatively low temperature and which gives a cured coating having a good finish appearance and excellent properties, and a method of curing the same.

These and other objects of the invention will become more apparent from the following description.

According to the invention, there are provided:

- (1) a curable resin composition comprising (I) at least one polysiloxane resin selected from the group consisting of (i) a polysiloxane resin which is a reaction product prepared by condensation of a silane compound (A) having at least one hydroxyl group and/or hydrolyzable group respectively directly attached to the silicon atom, the polysiloxane resin (i) having at least one hydroxyl group and/or hydrolyzable group respectively directly attached to the silicon atom on the average per molecule of the reaction product, and (ii) a polysiloxane resin which is a reaction product of the silane compound (A) having at least one hydroxyl group and/or hydrolyzable group respectively directly attached to the silicon atom with a silane compound (B) having at least one hydroxyl group and/or hydrolyzable group respectively directly attached to the silicon atom and at least one epoxy group, the polysiloxane resin (ii) having at least one hydroxyl group and/or hydrolyzable group

respectively directly attached to the silicone atom on the average and at least one epoxy group on the average, per molecule of the reaction product, and (II) a hydroxyl-containing resin or a hydroxyl- and carboxyl-containing resin; and (2) a method of curing the curable resin composition.

The present inventors conducted an extensive research to overcome the foregoing drawbacks of conventional curable compositions, and found that a curable resin composition comprising the above-specified polysiloxane resin and a hydroxyl-containing resin or a hydroxyl- and carboxyl-containing resin exhibits a high storage stability, is curable at a relatively low temperature and gives a cured coating which is outstanding in finish appearance and in other properties.

The present invention has been accomplished based on this novel finding.

The hydrolyzable group directly attached to the silicon atom is a residue capable of forming a hydroxysilane group on hydrolysis in the presence of water. Examples of such hydrolyzable groups are  $C_{1-5}$  alkoxyl; aryloxy groups such as phenoxy, tolyloxy, p-methoxyphenoxy, p-nitrophenoxy, benzyloxy, etc.; acyloxy groups such as acetoxy, propionyloxy, butanoyloxy, benzoyloxy, phenylacetoxy, formyloxy, etc.; and residues represented by the formulae

$-N(R_1)_2$ ,  $-ON(R_1)_2$ ,  $-ON=C(R_1)_2$  and  $-NR_2COR_1$  (wherein the  $R_1$  groups are the same or different and each represent a  $C_{1-8}$  alkyl group, an aryl group or an aralkyl group, and  $R_2$  is a hydrogen atom or a  $C_{1-8}$  alkyl group).

5        Of the polysiloxane resins for use as the component (I) in the invention, the resin (i) has a main skeleton formed of siloxane bond, and the hydroxyl group, hydrolyzable group, optionally hydrocarbon group, and the like are directly attached to the silicon atom of the main skeleton.  
10      The resin (ii) has epoxy group indirectly attached to the silicon atom having the foregoing groups of the resin (i) attached thereto.

      The polysiloxane resin (i) is obtained by hydrolysis and subsequent condensation of the silane compound (A). The  
15      polysiloxane resin (ii) is obtained by reacting the silane compound (A) with the epoxy-containing silane compound (B).

      The silane compound (A) has three hydroxyl and/or hydrolyzable groups on the average per molecule, as respectively directly attached to the silicon atom, and is  
20      preferably a compound represented by the formula



      wherein  $R_3$  is a hydrocarbon group and the groups  $Z$  are the same or different and each represent a hydrolyzable group or a hydroxyl group.

25      Preferred examples of  $R_3$  groups in the formula (1) are

a straight- or branched-chain aliphatic hydrocarbon group having 1 to 8 carbon atoms, aryl group, and aralkyl group. More preferred examples are a methyl group, phenyl group and phenethyl group. Examples of aliphatic hydrocarbon groups  
5 having 1 to 8 carbon atoms are methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, etc.

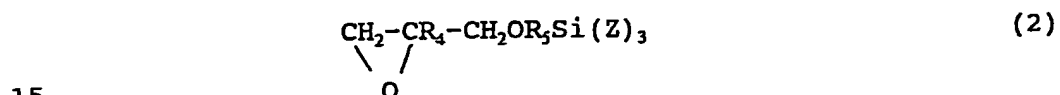
Preferred examples of Z groups are methoxy, ethoxy, propoxy, hydroxyl, acetoxy, etc. Preferred examples of the silane compound (A) are methyltrimethoxysilane,  
10 phenyltrimethoxysilane, phenethyltrimethoxysilane, butyltrimethoxysilane, methyltriethoxysilane, methyltributoxysilane, phenyltrisilanol, methyltrisilanol, methyltriacetoxysilane, phenyltriacetoxysilane, etc. Among them, more preferred are methyltrimethoxysilane,  
15 phenyltrimethoxysilane, phenethyltrimethoxysilane, phenyltrisilanol, methyltriacetoxysilane and phenyltriacetoxysilane, etc.

The trialkoxysilane compound or other compounds as mentioned above may be used conjointly with a dialkoxysilane  
20 compound and/or tetraalkoxysilane compound properly selected according to the required properties. Examples of useful dialkoxysilane compounds are dimethyldimethoxysilane, diethyldiethoxysilane, dipropyldipropoxysilane, diphenyldimethoxysilane, etc. Examples of the  
25 tetraalkoxysilane compounds are tetramethoxysilane,

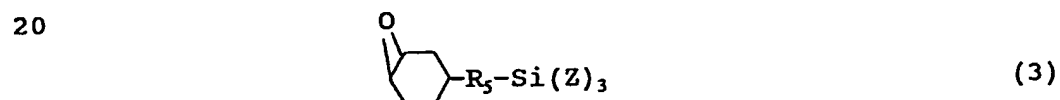
tetraethoxysilane, tetrapropoxysilane, dimethoxydipropoxy-silane, etc. The silane compound is used in an amount of about 20 mole% or less based on the combined amount of the silane compound (A) and the silane compound.

5        The epoxy-containing silane compound (B) is a monomer containing an average of three hydroxyl and/or hydrolyzable groups respectively directly attached to the silicon atom and an average of one epoxy group, per molecule. The epoxy groups may be either aliphatic or  
10        alicyclic.

Preferred examples of the epoxy-containing silane compound (B) are aliphatic epoxy-containing silane compounds represented by the formula



wherein  $R_1$  is a hydrogen atom or a methyl group,  $R_2$  is a  $C_{1-10}$  hydrocarbon group and Z means the same meaning as above; and alicyclic epoxy-containing silane compounds represented by the formula



wherein  $R_3$  and Z are as defined above. The above epoxy-containing silane compounds can be used singly or at least two of them are usable in mixture.

25        Preferred examples of Z groups are methoxy, ethoxy,

propoxy, hydroxyl, acetoxy, etc.

More specific examples of preferred epoxy-containing silane compound (B) are  $\gamma$ -glycidoxypropyltrimethoxysilane,  $\gamma$ -glycidoxypropyltriethoxysilane,  $\gamma$ -methylglycidoxypropyltrimethoxysilane,  $\delta$ -glycidoxybutyltriethoxysilane and like aliphatic epoxy-containing silane compounds,  $\beta$ (3,4-epoxycyclohexyl)ethyltrimethoxysilane and like alicyclic epoxy-containing silane compounds.

The hydrolysis-induced condensation reaction of the silane compound (A) for preparing the polysiloxane resin (i) is the condensation reaction (involving dehydration) of the hydroxyl groups formed by the hydrolysis of alkoxy silane groups and the like in the compound (A). In this case, condensation entailing elimination of alkoxy groups or the like as well as the condensation involving dehydration may occur depending on the reacting conditions.

It is desirable to effect the hydrolysis before the condensation. Generally the hydrolysis and condensation are caused by heating the reactants with stirring in an inactive organic solvent in the presence of water and a catalyst. The amount of water used is not specifically limited, preferably about 0.1 mole or more per mole of the alkoxy silane group. Use of less than 0.1 mole is likely to reduce the reaction efficiency. Acid catalysts are usable as the catalyst. Useful acid catalysts include, for



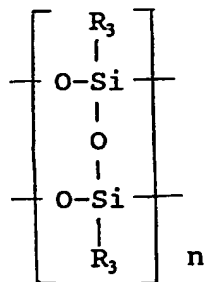
example, hydrochloric acid, sulfuric acid, phosphoric acid, formic acid, acetic acid, propionic acid, acrylic acid, methacrylic acid, etc. A suitable amount of the catalyst used is in the range of about 0.0001 to about 5 parts by weight, preferably about 0.01 to about 0.5 part by weight, per 100 parts by weight of the silane compound (A).

The reaction temperature is in the range of about 20 to about 180°C, preferably about 50 to about 120°C. A proper reaction time is in the range of about 1 to about 40 hours.

Examples of useful organic solvents are hydrocarbon solvents, ester solvents, ketone solvents, alcohol solvents, etc.

The main skeleton of the polysiloxane resin prepared by reacting the silane compound (A) is composed of siloxane bond. The main skeleton of the resin may be of the type having a ladder-like structure or of the mixed type comprising predominantly a ladder-like structure and partially a straight-chain structure.

Preferred ladder-like structures in the resin (i) contain structural units represented by the formula



wherein  $R_3$  is as defined above and  $n$  is an integer of not smaller than 2.

The polysiloxane resin (i) for use in the invention has an average of at least 1, preferably about 1 to about 50, hydroxyl groups and/or hydrolyzable groups respectively directly attached to the silicon atom, per molecule. If the number of these groups is less than one, the obtained curable composition is not excellent in curability at low temperatures. Reversely if the number of these groups is over 50, the cured product shows deteriorated water resistance. Thus the composition having these groups outside the range is undesirable.

The polysiloxane resin (i) has a number average molecular weight of about 400 to about 100,000, preferably about 500 to about 80,000. If the number average molecular weight is less than 400, it is difficult to form a ladder-like structure and an impaired storage stability results. Reversely the number average molecular weight of more than 100,000 reduces the compatibility with the component (II) and tends to lower the storage stability and to impair the appearance of the coating (gloss, surface smoothness, etc.). Thus the resin (i) having a number average molecular weight outside the above range is undesirable.

The polysiloxane resin (ii) for use in the invention can be prepared by reacting a mixture of the silane compound

(A) and the epoxy-containing silane compound (B). Desirable proportions are about 10 to about 99.9 mole%, preferably about 30 to about 99 mole%, of the silane compound (A) and about 90 to about 0.1 mole%, preferably about 70 to about 1 mole%, of the epoxy-containing silane compound (B), based on the combined amount of the two compounds. If the proportion of the silane compound (A) is less than 10 mole%, the epoxy content in the polysiloxane resin (ii) increases and the compatibility of the resin (ii) with the resin as the component (II) deteriorates, making it difficult to form a cured coating which is outstanding in finish appearance (gloss, surface smoothness, etc.) and in other properties (water resistance, etc.). Reversely if the proportion of the silane compound (A) is larger than 99.9 mole%, the epoxy content in the polysiloxane resin (ii) decreases and the curability at low temperatures is likely to reduce.

The reaction between the silane compound (A) and the epoxy-containing silane compound (B) is conducted by condensation (entailing dehydration) of the hydroxyl groups of the two compounds and the hydroxyl groups formed by hydrolysis of hydrolyzable groups. Condensation entailing elimination of hydrolyzable groups as well as the condensation involving dehydration takes place depending on the reacting conditions in this case.

If the resin has hydrolyzable group or groups directly

attached to the silicon atom, the hydrolyzable group may be preferably hydrolyzed prior to condensation. The hydrolysis and condensation are caused usually by heating the reactants with stirring in an inactive organic solvent in the presence of water and a catalyst. The amount of water used is not specifically limited, preferably about 0.1 mole or more per mole of the hydrolyzable group. Use of less than 0.1 mole of water is likely to diminish the reaction efficiency. Useful catalysts include acid catalysts such as hydrochloric acid, sulfuric acid, phosphoric acid, formic acid, acetic acid, propionic acid, acrylic acid, methacrylic acid, etc. A suitable amount of the catalyst used is in the range of about 0.0001 to about 5 parts by weight, preferably about 0.01 to about 0.5 part by weight, per 100 parts by weight of the combined amount of the silane compound (A) and the epoxy-containing silane compound (B).

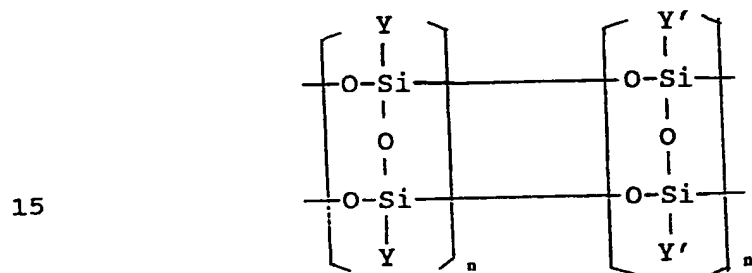
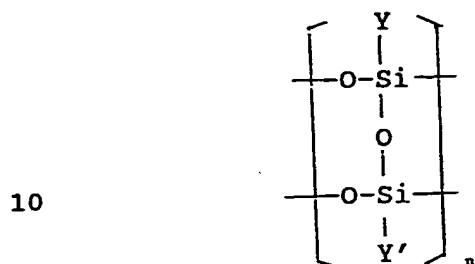
The reaction temperature is in the range of about 20 to about 180°C, preferably about 50 to about 120°C. A proper reaction time is in the range of about 1 to about 40 hours.


Examples of useful organic solvents are hydrocarbon solvents, ester solvents, ketone solvents, alcohol solvents, etc.

The polysiloxane resin (ii) prepared by reacting the silane compound (A) and the epoxy-containing silane compound (B) has a main skeleton formed of siloxane bond. The main

skeleton of the resin (ii) may be of the type having a ladder-like structure or of the mixed type formed of predominantly a ladder-like structure and partially a straight-chain structure.

5 Preferred ladder-like structures in the resin (ii) contain units represented by the formulae



wherein Y is R<sub>1</sub>, Y' is R<sub>3</sub>OCH<sub>2</sub>CR<sub>4</sub>CH<sub>2</sub> or R<sub>5</sub>-O, R<sub>1</sub>, R<sub>4</sub>

20 and R<sub>3</sub> are as defined above and n is an integer of not smaller than 2.

The polysiloxane resin (ii) for use in the invention has an average of at least one, preferably an average of about 1 to about 50, hydroxyl groups and/or hydrolyzable groups respectively directly attached to the silicon atom,

per molecule and an average of at least one, preferably an average of about 1 to about 50, epoxy groups, per molecule. If the numbers of hydroxyl groups and/or hydrolyzable groups respectively directly attached to the silicon atom and epoxy groups are less than the above ranges, it is difficult to obtain a curable composition of high curability at low temperatures.

The polysiloxane resin (ii) has a number average molecular weight of about 400 to about 100,000, preferably about 500 to about 80,000. If the resin (ii) has a number average molecular weight of less than 400, it is difficult to form a ladder-like structure and the storage stability decreases. Reversely the number average molecular weight of more than 100,000 reduces the compatibility with the component (II) and tends to impair the finish appearance of the coating (gloss, surface smoothness, etc.). Thus the resin (ii) having a number average molecular weight outside the above range is undesirable.

The hydroxyl-containing resin or hydroxyl- and carboxyl-containing resin as the component (II) to be conjointly used with the polysiloxane resin as the component (I) is suitably selected from conventional resins without specific limitation, and include, for example, vinyl-type resins, fluorine-containing resins, polyester-type resins, etc.

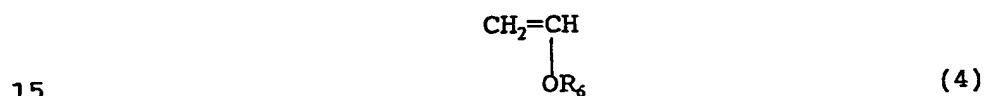
When the polysiloxane resin (i) is used as the component (I), it is preferred to use the hydroxyl-containing resin as the component (II) in combination.

Useful hydroxyl-containing resins include, for example, resins (1) to (5) stated below.

(1) Hydroxyl-containing vinyl-type resin

The resin is a polymer prepared from a hydroxyl-containing polymerizable unsaturated monomer (a) described below and, when required, another polymerizable unsaturated monomer (b) described below.

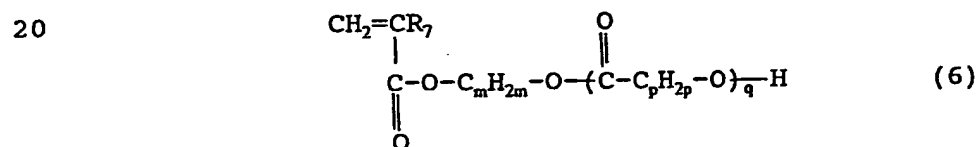
Examples of the hydroxyl-containing polymerizable unsaturated monomer (a) are compounds represented by the formulae (4) to (7) below



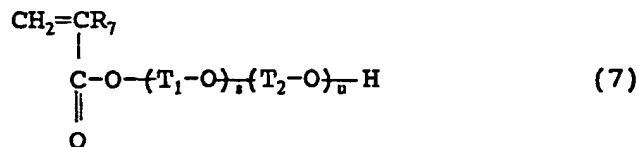
wherein  $R_6$  is a hydrogen atom or a hydroxyalkyl group,



wherein  $R_6$  is as defined above,



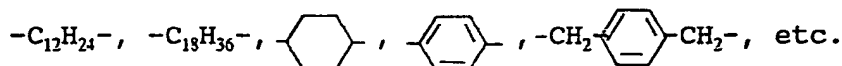
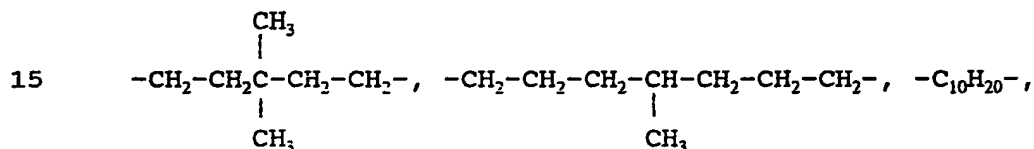
wherein  $R_7$  is a hydrogen atom or a methyl group,  $m$  is an integer of 2 to 8,  $p$  is an integer of 2 to 18, and  $q$  is an integer of 0 to 7,



wherein  $\text{R}_7$  is as defined above,  $\text{T}_1$  and  $\text{T}_2$  are the same or different and each represent a bivalent hydrocarbon group having 1 to 20 carbon atoms, and  $s$  and  $u$  are each an integer of 0 to 10, provided that the sum of  $s$  and  $u$  is 1 to 10.

The hydroxyalkyl group in the formulae (4) and (5) has 1 to 8 carbon atoms. Specific examples are  $-\text{C}_2\text{H}_4\text{OH}$ ,  $-\text{C}_3\text{H}_6\text{OH}$ ,  $-\text{C}_4\text{H}_8\text{OH}$ , etc.

Examples of  $\text{C}_{1-20}$  bivalent hydrocarbon groups in the formula (7) are  $-\text{CH}_2-$ ,  $-\text{CH}_2-\text{CH}_2-$ ,  $-\text{CH}_2-\text{CH}_2-\text{CH}_2-$ ,  $-\text{CH}_2-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_2-$ ,

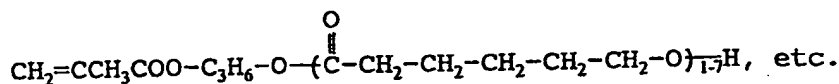


Examples of the monomer (a) of the formula (4) are  $\text{CH}_2=\text{CHOH}$ ,  $\text{CH}_2=\text{CHOC}_4\text{H}_8\text{OH}$ , etc.

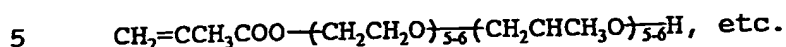
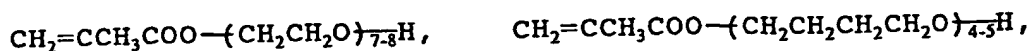
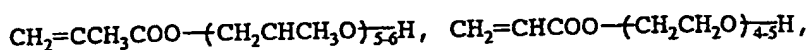
Examples of the monomer (a) of the formula (5) are  $\text{CH}_2=\text{CHCH}_2\text{OH}$ ,  $\text{CH}_2=\text{CHCH}_2\text{OCH}_2\text{CH}_2\text{OH}$ ,  $\text{CH}_2=\text{CHCH}_2\text{O}-(\text{CH}_2\text{CH}_2\text{O})_2\text{H}$ ,  $\text{CH}_2=\text{CHCH}_2\text{O}-(\text{CH}_2\text{CH}_2\text{O})_3\text{H}$ , etc.

Examples of the monomer (a) of the formula (6) are  $\text{CH}_2=\text{CHCOOC}_2\text{H}_4\text{OH}$ ,  $\text{CH}_2=\text{CCH}_3\text{COOC}_3\text{H}_6\text{OH}$ ,





Examples of the monomer (a) of the formula (7) are



Also usable as the monomer (a) is an adduct of any of hydroxyl-containing unsaturated monomers of the formulae (4) to (7) with a lactone such as  $\epsilon$ -caprolactone,  $\gamma$ -valerolactone or the like.

10 Polymerizable unsaturated monomer (b)

Monomers (b-1) to (b-7) given below are usable as the monomer (b):

(b-1) olefin-type compounds such as ethylene, propylene, butylene, isoprene, chloroprene, etc.;

15 (b-2) vinyl ethers and allyl ethers such as ethyl vinyl ether, propyl vinyl ether, isopropyl vinyl ether, butyl vinyl ether, tert-butyl vinyl ether, pentyl vinyl ether, hexyl vinyl ether, isohexyl vinyl ether, octyl vinyl ether, 4-methyl-1-pentyl vinyl ether and like chain-like alkyl  
20 vinyl ethers, cyclopentyl vinyl ether, cyclohexyl vinyl ether and like cycloalkyl vinyl ethers, phenyl vinyl ether, o-, m-, p-trivinyl ether and like aryl vinyl ethers, benzyl vinyl ether, phenethyl vinyl ether, and like aralkyl vinyl ethers, etc.;

25 (b-3) vinyl esters and propenyl esters such as vinyl

acetate, vinyl lactate, vinyl butyrate, vinyl isobutyrate, vinyl caproate, vinyl isocaproate, vinyl pivalate, vinyl caprate and like vinyl esters, isopropenyl acetate, isopropenyl propionate and like propenyl esters, etc.;

5 (b-4) esters of acrylic or methacrylic acids such as methyl acrylate, ethyl acrylate, propyl acrylate, isopropyl acrylate, butyl acrylate, hexyl acrylate, octyl acrylate, lauryl acrylate, methyl methacrylate, ethyl methacrylate, propyl methacrylate, isopropyl methacrylate, butyl  
10 methacrylate, hexyl methacrylate, octyl methacrylate, lauryl methacrylate and like alkyl (having 1 to 18 carbon atoms) esters of acrylic or methacrylic acids; methoxybutyl acrylate, methoxybutyl methacrylate, methoxyethyl acrylate, methoxyethyl methacrylate, ethoxybutyl acrylate, ethoxybutyl  
15 methacrylate and like alkoxyalkyl (having 2 to 18 carbon atoms) esters of acrylic or methacrylic acids, etc.;

(b-5) vinyl aromatic compounds such as styrene,  $\alpha$ -methyl styrene, vinyl toluene, p-chlorostyrene, etc.;

(b-6) carboxyl-containing polymerizable unsaturated monomers  
20 such as acrylic acid, methacrylic acid, crotonic acid, itaconic acid, maleic acid, maleic anhydride, fumaric acid, 2-carboxyethyl (meth)acrylate, 3-carboxypropyl (meth)acrylate, 5-carboxypentyl (meth)acrylate, etc.;

(b-7) others such as acrylonitrile, methacrylonitrile, etc.

25 (2) Hydroxyl- and fluorine-containing resin

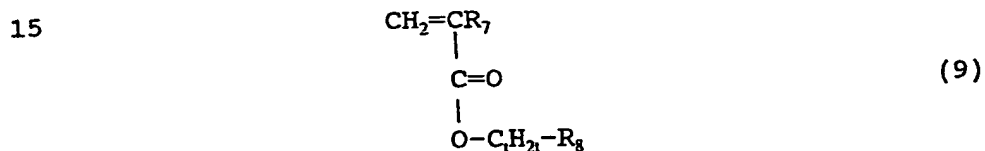
The resin is a polymer prepared from the hydroxyl-containing polymerizable unsaturated monomer (a), a fluorine-containing polymerizable unsaturated monomer (c) and, when required, the polymerizable unsaturated monomer (b).

Fluorine-containing polymerizable unsaturated monomer (c)

Examples of the monomer (c) are compounds represented by the formulae (8) and (9) below:



wherein the X groups are the same or different and each represent a hydrogen atom, a chlorine atom, a bromine atom, a fluorine atom, an alkyl group or a haloalkyl group, provided that at least one fluorine atom is contained in the formula



wherein  $R_7$  is as defined above,  $R_8$  is a fluoroalkyl group and  $t$  is an integer of 1 to 10.

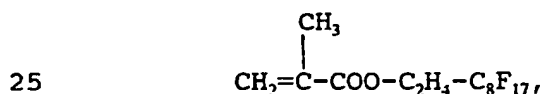
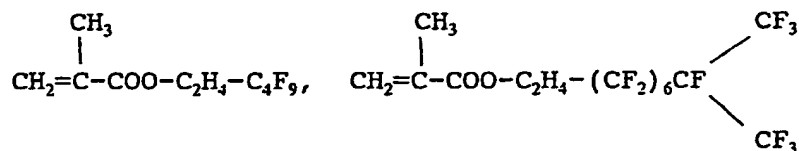
The alkyl group in the formula (8) has 1 to 6 carbon atoms, preferably 1 to 4 carbon atoms. Examples are methyl, ethyl, propyl, isopropyl, butyl, pentyl, etc. The haloalkyl group in the formula (8) has 1 to 6 carbon atoms, preferably 1 to 4 carbon atoms. Examples are  $CF_3$ ,  $CHF_2$ ,  $CH_2F$ ,  $CCl_3$ ,  $CHCl_2$ ,  $CH_2Cl$ ,  $CFCl_2$ ,  $(CF_2)_2CF_3$ ,  $(CF_2)_3CF_3$ ,  $CF_2CH_3$ ,  $CF_2CHF_2$ ,

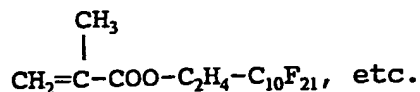
$\text{CF}_2\text{Br}$ ,  $\text{CH}_2\text{Br}$ , etc.

Examples of the monomer of the formula (8) are as follows:  $\text{CF}_2=\text{CF}_2$ ,  $\text{CHF}=\text{CF}_2$ ,  $\text{CH}_2=\text{CF}_2$ ,  $\text{CH}_2=\text{CHF}$ ,  $\text{CClF}=\text{CF}_2$ ,  $\text{CHCl}=\text{CF}_2$ ,  $\text{CCl}_2=\text{CF}_2$ ,  $\text{CClF}=\text{CClF}$ ,  $\text{CHF}=\text{CCl}_2$ ,  $\text{CH}_2=\text{CClF}$ ,  $\text{CCl}_2=\text{CClF}$ ,  $\text{CF}_3\text{CF}=\text{CF}_2$ ,  $\text{CF}_3\text{CF}=\text{CHF}$ ,  $\text{CF}_3\text{CH}=\text{CF}_2$ ,  $\text{CF}_3\text{CF}=\text{CH}_2$ ,  $\text{CHF}_2\text{CF}=\text{CHF}$ ,  $\text{CH}_3\text{CF}=\text{CF}_2$ ,  $\text{CH}_3\text{CF}=\text{CH}_2$ ,  $\text{CF}_2\text{ClCF}=\text{CF}_2$ ,  $\text{CF}_3\text{CCl}=\text{CF}_2$ ,  $\text{CF}_3\text{CF}=\text{CFCl}$ ,  $\text{CF}_2\text{ClCCl}=\text{CF}_2$ ,  $\text{CF}_2\text{ClCF}=\text{CFCl}$ ,  $\text{CFCl}_2\text{CF}=\text{CF}_2$ ,  $\text{CF}_2\text{CCl}=\text{CClF}$ ,  $\text{CF}_3\text{CCl}=\text{CCl}_2$ ,  $\text{CClF}_2\text{CF}=\text{CCl}_2$ ,  $\text{CCl}_3\text{CF}=\text{CF}_2$ ,  $\text{CF}_2\text{ClCCl}=\text{CCl}_2$ ,  $\text{CFCl}_2\text{CCl}=\text{CCl}_2$ ,  $\text{CF}_3\text{CF}=\text{CHCl}$ ,  $\text{CClF}_2\text{CF}=\text{CHCl}$ ,  $\text{CF}_3\text{CCl}=\text{CHCl}$ ,  $\text{CHF}_2\text{CCl}=\text{CCl}_2$ ,  $\text{CF}_2\text{ClCH}=\text{CCl}_2$ ,  $\text{CF}_2\text{ClCCl}=\text{CHCl}$ ,  $\text{CCl}_3\text{CF}=\text{CHCl}$ ,  $\text{CF}_2\text{ClCF}=\text{CF}_2$ ,  $\text{CF}_2\text{BrCH}=\text{CF}_2$ ,  $\text{CF}_3\text{CBr}=\text{CHBr}$ ,  $\text{CF}_2\text{ClCBr}=\text{CH}_2$ ,  $\text{CH}_2\text{BrCF}=\text{CCl}_2$ ,  $\text{CF}_3\text{CBr}=\text{CH}_2$ ,  $\text{CF}_2\text{CH}=\text{CHBr}$ ,  $\text{CF}_2\text{BrCH}=\text{CHF}$ ,  $\text{CF}_2\text{BrCF}=\text{CF}_2$ ,  $\text{CF}_3\text{CF}_2\text{CF}=\text{CF}_2$ ,  $\text{CF}_3\text{CF}=\text{CFCF}_3$ ,  $\text{CF}_3\text{CH}=\text{CFCF}_3$ ,  $\text{CF}_2=\text{CFCF}_2\text{CHF}_2$ ,  $\text{CF}_3\text{CF}_2\text{CF}=\text{CH}_2$ ,  $\text{CF}_3\text{CH}=\text{CHCF}_3$ ,  $\text{CF}_2=\text{CFCF}_2\text{CH}_3$ ,  $\text{CF}_2=\text{CFCH}_2\text{CH}_3$ ,  $\text{CF}_3\text{CH}_2\text{CH}=\text{CH}_2$ ,  $\text{CF}_3\text{CH}=\text{CHCH}_3$ ,  $\text{CF}_2=\text{CHCH}_2\text{CH}_3$ ,  $\text{CH}_3\text{CF}_2\text{CH}=\text{CH}_2$ ,  $\text{CFH}_2\text{CH}=\text{CHCFH}_2$ ,  $\text{CH}_3\text{CF}_2\text{CH}=\text{CH}_2$ ,  $\text{CH}_2=\text{CFCH}_2\text{CH}_3$ ,  $\text{CF}_3(\text{CF}_2)_2\text{CF}=\text{CF}_2$ ,  $\text{CF}_3(\text{CF}_2)_3\text{CF}=\text{CF}_2$ , etc.

The fluoroalkyl group in the formula (9) has 3 to 21 carbon atoms. Examples are  $\text{C}_4\text{F}_9$ ,  $(\text{CF}_2)_6\text{CF}(\text{CF}_3)_2$ ,  $\text{C}_8\text{F}_{17}$ ,  $\text{C}_{10}\text{F}_{21}$ , etc.

Examples of the monomer of the formula (9) are





(3) Hydroxyl-containing polyester resin

The resin can be prepared by esterification reaction or transesterification reaction of a polybasic acid with a polyhydric alcohol. Examples of useful polybasic acids are compounds containing 2 to 4 carboxyl groups or methyl carboxylate groups per molecule, such as phthalic acid (anhydride), isophthalic acid, terephthalic acid, maleic acid (anhydride), pyromellitic acid (anhydride), trimellitic acid (anhydride), succinic acid (anhydride), sebacic acid, azelaic acid, dodecanedicarboxylic acid, dimethyl isophthalate, dimethyl terephthalate, etc. Examples of useful polyhydric alcohols are alcohols containing 2 to 6 hydroxyl groups per molecule, such as ethylene glycol, polyethylene glycol, propylene glycol, neopentyl glycol, 1,6-hexanediol, trimethylolpropane, pentaerythritol, glycerin, tricyclodecanedimethanol, etc. Also usable, when required, are monobasic acids such as castor oil fatty acid, soy bean oil fatty acid, tall oil fatty acid, linseed oil fatty acid and like fatty acids, and benzoic acid, etc.

(4) Hydroxyl-containing polyurethane resin

The resin is an isocyanate-free one prepared by modifying a resin (such as hydroxyl-containing vinyl-type resin, hydroxyl- and fluorine-containing resin, hydroxyl-

containing polyester resin, etc.) with a polyisocyanate compound (such as tolylene diisocyanate, xylene diisocyanate, hexamethylene diisocyanate, isophorone diisocyanate, etc.).

- 5 (5) Resin prepared by partially or wholly hydrolyzing a polyvinyl acetate or a copolymer prepared from a vinyl acetate and another polymerizable unsaturated monomer.

The above hydroxyl-containing resin has a number average molecular weight of about 1,000 to about 100,000, preferably about 2,000 to about 80,000. If the resin has a number average molecular weight of less than 1,000, the cured coating exhibits lower impact resistance, lower water resistance and other impaired properties. If the resin has a number average molecular weight of more than 100,000, the compatibility and other properties are impaired. Thus the hydroxyl-containing resin having a number average molecular weight outside the above range is undesirable.

The resin has an average of one or more hydroxyl groups, preferably an average of about 2 to about 100 hydroxyl groups, per molecule. The resin having less than one hydroxyl group is undesirable because the use of such resin reduces the curability and makes it difficult to obtain a coating which is excellent in properties (such as water resistance, impact resistance, etc.).

25 When the polysiloxane resin (ii) is used as the

component (I), it is desirable to use a hydroxyl- and carboxyl-containing resin as the component (II) in combination.

Examples of such hydroxyl- and carboxyl-containing resins are as follows.

(1) Hydroxyl- and carboxyl-containing vinyl-type resins

A copolymer prepared from the hydroxyl-containing polymerizable unsaturated monomer (a), a carboxyl-containing polymerizable unsaturated monomer (d) and, when required, the polymerizable unsaturated monomer (b).

Carboxyl-containing polymerizable unsaturated monomer (d)

Usable as such monomers are compounds represented by the formulae (10) and (11) below.



wherein  $R_{11}$  is a hydrogen atom or a lower alkyl group,  $R_{12}$  is a hydrogen atom, a lower alkyl group, or a carboxyl group, and  $R_{13}$  is a hydrogen atom, a lower alkyl group, or a carboxyl lower alkyl group, and



wherein  $R_{14}$  is a hydrogen atom or a methyl group, and  $m$  is as defined above.

Preferred lower alkyl groups in the formula (10) are

those having 4 or less carbon atoms, and methyl is more preferred.

Examples of the compound of the formula (10) are acrylic acid, methacrylic acid, crotonic acid, itaconic acid, maleic acid, maleic anhydride, fumaric acid, etc.

Examples of the compound of the formula (11) are 2-carboxyethyl (meth)acrylate, 3-carboxypropyl (meth)acrylate, 5-carboxypentyl (meth)acrylate, etc.

Also usable as the monomer (d) is an adduct prepared by subjecting to addition reaction 1 mole of the hydroxyl-containing polymerizable unsaturated monomer (a) and 1 mole of a carboxylic anhydride compound (e.g., maleic anhydride, itaconic anhydride, succinic anhydride, phthalic anhydride, etc.).

(2) Hydroxyl-, carboxyl- and fluorine-containing resin

The resin is a copolymer prepared from the hydroxyl-containing polymerizable unsaturated monomer (a), fluorine-containing polymerizable unsaturated monomer (c), carboxyl-containing polymerizable unsaturated monomer (d) and, when required, the polymerizable unsaturated monomer (b).

(3) Hydroxyl- and carboxyl-containing polyester resin

The resin is prepared, for example, by esterification reaction or transesterification reaction of a polybasic acid with a polyhydric alcohol or prepared by subjecting to addition reaction the obtained hydroxyl-containing polyester



resin and an acid anhydride. Examples of useful polybasic acids are compounds containing 2 to 4 carboxyl groups or methyl carboxylate groups per molecule, such as phthalic acid (anhydride), isophthalic acid, terephthalic acid, maleic acid (anhydride), pyromellitic acid (anhydride), trimellitic acid (anhydride), succinic acid (anhydride), sebacic acid, azelaic acid, dodecanedicarboxylic acid, dimethyl isophthalate, dimethyl terephthalate, etc. Examples of useful polyhydric alcohols are alcohols containing 2 to 6 hydroxyl groups per molecule, such as ethylene glycol, polyethylene glycol, propylene glycol, neopentyl glycol, 1,6-hexanediol, trimethylolpropane, pentaerythritol, glycerin, tricyclodecanedimethanol, etc. Also usable are monobasic acids such as castor oil fatty acid, soy bean oil fatty acid, tall oil fatty acid, linseed oil fatty acid and like fatty acids, and benzoic acid, etc., when so required.

The hydroxyl- and carboxyl-containing resin has a number average molecular weight of about 1,000 to about 100,000, preferably about 2,000 to about 80,000. If the resin has a number average molecular weight less than 1,000, reduced curability results and the cured coating is deteriorated in impact resistance, etc. On the other hand, if the number average molecular weight of the resin is more than 100,000, the compatibility is impaired and the

appearance of coating surface and other properties are deteriorated. Thus the resin having a number average molecular weight outside the above range is undesirable.

5 The resin preferably has an average of one or more hydroxyl groups and one or more carboxyl groups, preferably an average of about 2 to about 100 respective groups, per molecule. The resin having these groups which average less than one is undesirable because the use of such resin reduces the curability and makes it difficult to obtain a  
10 coating which is excellent in properties (such as water resistance, impact resistance, etc.).

The mixing ratio of the polysiloxane resin (I) to the hydroxyl- or hydroxyl- and carboxyl-containing resin (II) is in the range of between about 5/95 and about 95/5,  
15 preferably between about 20/80 and about 80/20. If the resins (I) and (II) are used in a ratio outside said range, the composition is rendered less curable, and a coating excellent in properties (such as water resistance, impact resistance, etc.) is difficult to form.

20 While the curable composition of the invention is fully cured by heating, e.g. at about 80°C or higher, the curing composition of the invention containing a curing catalyst is curable at a low temperature or capable of drying at ambient temperature.

25 Curing catalysts which can be used in the invention are

described below.

(1) Metal chelate compound

Preferred metal chelate compounds are, for example, aluminum chelate compounds, titanium chelate compounds, zirconium chelate compounds, etc. Among them, more preferred are chelate compounds containing a compound capable of forming a keto-enol tautomer as ligands capable of forming a stable chelate ring.

Examples of useful compounds capable of forming a keto-enol tautomer are  $\beta$ -diketones (acetylacetone, etc.), acetoacetates (methyl acetoacetate, etc.), malonates (ethyl malonate, etc.), ketones having a hydroxyl group in the  $\beta$  position (diacetone alcohol, etc.), aldehydes having a hydroxyl group in the  $\beta$  position (salicylaldehyde, etc.), esters having a hydroxyl group in the  $\beta$  position (methyl salicylate), etc. Good results can be obtained by use of acetoacetate,  $\beta$ -diketone or the like.

The aluminum chelate compound can be prepared suitably, for example, by admixing the compound capable of forming a keto-enol tautomer with an aluminum alkoxide represented by the formula



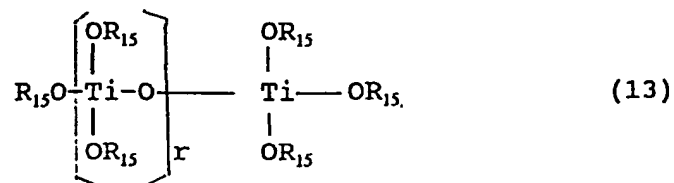
wherein the  $\text{R}_{15}$  groups are the same or different and each represent an alkyl group having 1 to 20 carbon atoms or an

alkenyl group, usually in the ratio of up to 3 moles of the former per mole of the latter, followed by heating when required.

5 Examples of alkyl groups having 1 to 20 carbon atoms in the formula (12) include undecyl, dodecyl, tridecyl, tetradecyl, octadecyl, etc. in addition to the aforesaid examples of alkyl groups having 1 to 10 carbon atoms. Examples of alkenyl groups in the formula (12) are vinyl, allyl, etc.

10 Examples of aluminum alcolates of the formula (12) are aluminum trimethoxide, aluminum dimethoxyethoxide, aluminum triethoxide, aluminum tri-n-propoxide, aluminum triisopropoxide, aluminum tri-n-butoxide, aluminum triisobutoxide, aluminum tri-sec-butoxide, aluminum tri-tert-butoxide, etc. among which aluminum triisopropoxide, 15 aluminum tri-sec-butoxide, aluminum tri-n-butoxide, etc. are preferred.

The titanium chelate compound can be prepared advantageously, for example, by admixing the compound 20 capable of forming a keto-enol tautomer with a titanate represented by the formula

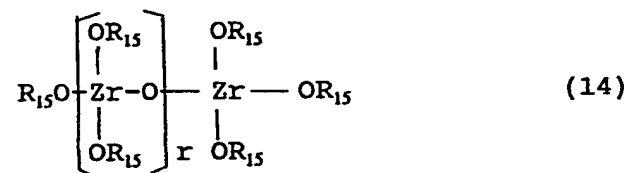


25 wherein r is an integer of 0 to 10 and R<sub>15</sub> is as defined

above, usually in the ratio of up to 4 moles of the former per mole of the Ti in the titanate, followed by heating when required.

Examples of the titanate of the formula (13) wherein r is 0 are tetramethyl titanate, tetraethyl titanate, tetra-n-propyl titanate, tetraisopropyl titanate, tetra-n-butyl titanate, tetra-isobutyl titanate, tetra-tert-butyl titanate, tetra-n-pentyl titanate, tetra-n-hexyl titanate, tetraisooctyl titanate, tetra-n-lauryl titanate, etc. Among them, tetraisopropyl titanate, tetra-n-butyl titanate, tetraisobutyl titanate, tetra-tert-butyl titanate, etc. give good results. Of the titanates wherein r is 1 or more, the dimers to hendecamers (r=1 to 10 in the formula (13)) of tetraisopropyl titanate, tetra-n-butyl titanate, tetraisobutyl titanate or tetra-tert-butyl titanate achieve good results.

The zirconium chelate compound can be prepared favorably, for example, by admixing the compound capable of forming a keto-enol tautomer with a zirconate represented by the formula



wherein r and  $R_{15}$  are as defined above, usually in the ratio of up to 4 moles of the former per mole of Zr in the

zirconate, followed by heating when required.

Examples of the zirconates of the formula (14) wherein r is 0 are tetraethyl zirconate, tetra-n-propyl zirconate, tetraisopropyl zirconate, tetra-n-butyl zirconate, tetra-sec-butyl zirconate, tetra-tert-butyl zirconate, tetra-n-pentyl zirconate, tetra-tert-pentyl-zirconate, tetra-tert-hexyl zirconate, tetra-n-heptyl zirconate, tetra-n-octyl zirconate, tetra-n-stearyl zirconate, etc. Among them, good results can be obtained by use of tetra-isopropyl zirconate, tetra-n-propyl zirconate, tetra isobutyl zirconate, tetra-n-butyl zirconate, tetra-sec-butyl zirconate, tetra-tert butyl zirconate or the like. Of these zirconates wherein r is 1 or more, the dimers to hendecamers (r =1 to 10 in the formula (14)) of tetra-isopropyl zirconate, tetra-n-propyl zirconate, tetra-n-butyl zirconate, tetra-isobutyl zirconate, tetra-sec-butyl zirconate or tetra-tert-butyl zirconate give good results. The chelate compound may contain structural units wherein such zirconates are associated with each other.

Preferred chelate compounds in the invention are aluminum chelate compounds such as tris(ethyl acetoacetate)-aluminum, tris(n-propylacetoacetate)aluminum, tris(isopropylacetoacetate)-aluminum, tris(n-butylacetoacetate)-aluminum, isopropoxybis-(ethylacetoacetate)aluminum, diisopropoxyethylacetoacetate aluminum, tris(acetyl-

acetonato)aluminum, tris(propionylacetonato)aluminum,  
diisopropoxypropionylacetonato aluminum, acetylacetonato-  
bis(propionylacetonato)aluminum, monoethylacetoacetate-  
bis(acetylacetonato)aluminum, tris(acetylacetonato)alu-  
minum, etc.; titanium chelate compounds such as diiso-  
propoxy-bis(ethylacetoacetate)titanate, diisopropoxy-  
bis(acetylacetonato)titanate, etc.; and zirconium chelate  
compounds such as tetrakis(acetylacetonato)zirconium,  
tetrakis(n-propylacetoacetate)zirconium, tetrakis(acetyl-  
acetonato)zirconium, tetrakis(ethylacetoacetate)zirconium,  
etc.

### (2) Lewis acid

Useful Lewis acids include, for example, metal halides,  
compounds having metal, halogen and other substituents, and  
complex salts of these compounds. Specific examples of such  
compounds are  $\text{AlCl}_3$ ,  $\text{AlCF}_3$ ,  $\text{AlF}_3$ ,  $\text{AlC}_2\text{H}_5\text{Cl}_2$ ,  $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ ,  $\text{SnCl}_4$ ,  
 $\text{TiCl}_4$ ,  $\text{TiBr}_4$ ,  $\text{TiF}_4$ ,  $\text{ZrCl}_4$ ,  $\text{ZrBr}_4$ ,  $\text{ZrF}_4$ ,  $\text{SnCl}_4$ ,  $\text{FeCl}_3$ ,  $\text{SbCl}_3$ ,  
 $\text{SbCl}_5$ ,  $\text{PCl}_3$ ,  $\text{PCl}_5$ ,  $\text{GaCl}_3$ ,  $\text{GaF}_3$ ,  $\text{InF}_3$ ,  $\text{BCl}_3$ ,  $\text{BBr}_3$ ,  $\text{BF}_3$ ,  
 $\text{BF}_3:(\text{OC}_2\text{H}_5)_2$ ,  $\text{BF}_4:(\text{OC}_2\text{H}_5)_3$ ,  $\text{BCl}_3:(\text{OC}_2\text{H}_5)_2$ ,  $\text{BF}_3:\text{NH}_2\text{C}_2\text{H}_5$ ,  $\text{BF}_3:\text{NH}_2\text{C}_2\text{H}_4\text{OH}$ ,  
 $\text{BF}_3:\text{NHCH}_2\text{CH}_2\text{CH}_2\text{CH}_2$ ,  $\text{PF}_6\text{S}-(\text{C}_6\text{H}_5)_3$ , etc.

### (3) Protonic acid

Specific examples of useful protonic acids are  
methanesulfonic acid, ethanesulfonic acid,  
trifluoromethanesulfonic acid, benzenesulfonic acid, p-  
toluenesulfonic acid and like organic protonic acids,

phosphoric acid, phosphorous acid, phosphinic acid, phosphonic acid, sulfuric acid, perchloric acid and like inorganic protonic acids, etc.

(4) Metal alkoxide

5           Specific examples of metal alkoxides are aluminum alkoxide, titanium alkoxide, zirconium alkoxide, etc.

          Also usable are compounds containing metal such as iron, calcium, barium or the like having attached thereto an alkoxy group, preferably a C<sub>1-18</sub>alkoxy group. These compounds  
10       may be associated with each other.

(5) Organic metal compound

          Specific examples of organic metal compounds are triethyl aluminum, zinc diethyl, etc.

(6) Compound having Si-O-Al bond or bonds

15           Such compounds include, for example, aluminum silicate.

          A suitable amount of the curing catalyst is about 0.01 to about 30 parts by weight per 100 parts by weight of the combined amount of the resins (I) and (II), calculated as solids. Amounts outside this range are undesirable because  
20       less than 0.01 part by weight used tends to reduce the curability, and more than 30 parts by weight used tends to remain in the cured coating and to decrease the water resistance. A preferred amount of the curing catalyst is about 0.01 to about 10 parts by weight and a more preferred  
25       one is about 0.5 to about 5 parts by weight.



Among the foregoing catalysts, preferred are metal chelate compounds which are outstanding in storage stability and in low temperature curability.

When required, the curable composition of the present invention may contain coloring pigments, extender pigments, UV absorbers, anti-oxidants, light stabilizers, water and organic solvents. Examples of organic solvents are ketone solvents, ester solvents, ether solvents, alcohol solvents, aliphatic hydrocarbon solvents, aromatic hydrocarbon solvents, etc.

The curable composition of the invention can be used as a component or an additive for coating compositions, printing inks, laminate materials, molding materials, adhesives, surface-treating agents, impregnating agents (for papers, fibers, concrete, etc.) and so on.

The curable composition of the invention is applied to a substrate made of an inorganic material (such as aluminum, iron, copper, zinc and like metals, glass, concrete, etc.) or an organic material (such as paper, fibers, plastics, etc.) by coating, printing or immersion, and then the coated substrate is cured by standing at room temperature or by baking e.g. at about 80 to about 300°C for about 5 to about 180 minutes.

The curable composition of the invention comprises the specific polysiloxane resin and the hydroxyl-containing

resin or the hydroxyl- and carboxyl-containing resin as the resin components. Thus the composition has the following advantages.

- (1) The composition has an excellent storage stability.
- 5 (2) The composition is cured uniformly in the surface and in the interior, giving a cured coating with outstanding aesthetic properties (glossy, shrink-free, etc.), and excellent properties (mechanical properties, etc.).
- (3) Even if cured at low temperatures, the composition gives  
10 a cured coating which is excellent in chemical resistance, water resistance, weatherability, abrasion resistance, water repellency, staining resistance, etc.

The present invention will be described below in more detail with reference to the following Examples and Comparison Examples in which parts and percentages are all by weight.

(i) Preparation of polysiloxane resin [A]

Phenyltrimethoxysilane	1980 parts
Deionized water	540 parts
20 30% Hydrochloric acid	1 part
Xylene	1560 parts

A mixture of the foregoing ingredients was subjected to condensation reaction at 80°C for 4 hours and then concentrated until the solids content thereof reached 50%. The  
25 polysiloxane obtained had a number average molecular weight

of 1,400 and 4 silanol groups on the average per molecule.  
Preparation of alkoxysilane group-containing resin [B] for  
comparison

To 100 parts of a mixture of the equal quantities of  
5 xylene and n-butanol was added dropwise a mixture of 55  
parts of n-butyl methacrylate, 15 parts of styrene, 30 parts  
of  $\gamma$ -methacryloxypropyltrimethoxysilane and 2 parts of  
azobisisobutyronitrile at 110°C over a period of 3 hours.  
The resulting mixture was copolymerized at the same tempera-  
10 ture for 2 hours, giving a resin [B] solution. The resin  
solution had a solids content of 50% and the resin had a  
number average molecular weight of 20,000.

Preparation of hydroxyl group-containing resin [C]

A resin solution was prepared in the same manner as in  
15 preparation of the above resin [B] using 100 parts of a  
mixture of the equal quantities of xylene and n-butanol, and  
a mixture of 70 parts of n-butyl methacrylate, 15 parts of  
styrene, 18 parts of 2-hydroxyethyl acrylate and 2 parts of  
azobisisobutyronitrile. The resin solution thus obtained  
20 had a solids content of 50%, and the resin had a number  
average molecular weight of 20,000 and a hydroxyl value of  
87 mg KOH/resin portion (calculated as solids) (corresponding  
to about 31 hydroxyl groups on the average per molecule).

#### Example 1

25 A 100 parts quantity of polysiloxane resin [A] solu-

tion, 100 parts of a hydroxyl group-containing resin [C] solution and 1 part of tris(acetylacetonato)aluminum were mixed together, giving a composition of Example 1.

Example 2

5           A 40 parts quantity of a polysiloxane resin [A] solution, 160 parts of a hydroxyl-group containing resin [C] solution and 1 part of tris(ethylacetoacetate)aluminum were mixed together, giving a composition of Example 2.

Comparison Example 1

10           A 100 parts quantity of an alkoxysilane group-containing resin [B] solution was mixed with 100 parts of a hydroxyl group-containing resin [C] solution, giving a composition of Comparison Example 1.

15           Table 1 shows the storage stabilities and film properties of the compositions obtained in Examples and Comparison Example.

Table 1

	Example 1	Example 2	Comparison Example 1
Storage stability	2 weeks	1	7
	2 months	1	50 <
Appearance and properties	Appearance of film	Satisfactory	Dulling, Shrinkage
	Gel fraction ratio	87	60
	Impact resistance	50 <	20
	Water resistance	Satisfactory	Blushing

The test methods employed in Examples 1 and 2 and Comparison Example 1 were as follows.

Storage stability: The compositions of Examples and Comparison Example which were adjusted to 1 poise in viscosity with xylene and n-butanol were each placed into a bottle for containing mayonnaise so that the composition in the bottle was half-full. The composition was allowed to stand at 40°C for a predetermined period of time and the variation of the viscosity, i.e. (viscosity after storage (poise))/(viscosity before storage (poise)) was checked.

#### Production of films

Each composition was applied to a substrate to a dry film thickness of 30  $\mu\text{m}$  and the coated substrate was baked at 140°C for 30 minutes, giving a film.

Appearance of film: Polished mild steel sheet was used as a substrate. The substrate was checked for undesirable change (dulling, shrinkage, cracking, peeling) on the surface thereof.

Gel fraction ratio: The film dried was removed from the glass plate and extracted by Soxhlet extractor at a reflux temperature for 6 hours using acetone. The remaining portion of the film was expressed in percentages by weight.

Impact resistance: Mild steel sheet was used as a substrate. With use of Du Pont impact tester, a weight of 500 g was dropped on the coated surface and the maximum height

(cm) at which the dropping caused no crack or peeling of the film was determined.

Water resistance: Mild steel sheet was used as a substrate. Test piece was immersed in warm water (40°C) for 40 days and then the film was checked for undesirable changes.

(ii-1) Preparation of polysiloxane [D]

	Methyltrimethoxysilane	1360 parts
	$\beta$ -(3,4-Epoxy cyclohexyl)-ethyltrimethoxysilane	246 parts
10	Deionized water	594 parts
	30% Hydrochloric acid	1 part
	Toluene	572 parts
	Isobutyl acetate	572 parts

A mixture of the above ingredients was subjected to condensation reaction at 74°C for 3 hours and then concentrated until the solids content thereof reached 50%. The obtained polysiloxane had a number average molecular weight of 6000 and 7 epoxy groups and 4 silanol groups on the average per molecule.

(ii-2) Preparation of polysiloxane [E]

	Phenyltrimethoxysilane	990 parts
	$\beta$ -(3,4-Epoxy cyclohexyl)-ethyltrimethoxysilane	246 parts
	Deionized water	324 parts
25	30% Hydrochloric acid	0.6 part
	Xylene	984 parts

A mixture of the above ingredients was subjected to condensation reaction at 80°C for 5 hours and then concentrated until the solids content thereof reached 50%. The polysiloxane obtained was 1650 in number average molecular weight and had 2 epoxy groups and 4 silanol groups on the average per molecule.

(ii-3) Preparation of polysiloxane [F]

	Phenyltrimethoxysilane	990 parts
	$\gamma$ -Glycidylpropyltrimethoxysilane	236 parts
10	Deionized water	324 parts
	30% Hydrochloric acid	0.6 part
	Xylene	984 parts

A mixture of the foregoing ingredients was subjected to condensation reaction at 80°C for 4 hours and then concentrated until the solids content thereof reached 50%. The polysiloxane obtained was 1140 in number average molecular weight and had 1.4 epoxy groups and 4 silanol groups on the average per molecule.

(ii-4) Preparation of polysiloxane [G]

20	Phenethyltrimethoxysilane	678 parts
	$\gamma$ -Glycidylpropyltrimethoxysilane	236 parts
	Deionized water	216 parts
	30% Hydrochloric acid	0.5 part
	Xylene	746 parts

A mixture of the above ingredients was subjected to



condensation reaction at 80°C for 5 hours and then concentrated until the solids content thereof reached 50%. The polysiloxane thus obtained was 1300 in number average molecular weight and had 2 epoxy groups and 4 silanol groups on the average per molecule.

Preparation of hydroxyl group- and carboxyl group-containing resin [H]

	n-Butyl methacrylate	63.4 parts
	Styrene	15 parts
10	2-Hydroxyethyl acrylate	18 parts
	Acrylic acid	3.6 parts
	Azobisisobutyronitrile	2 parts

A mixture of the above ingredients was added dropwise to 100 parts of a mixture of the equal quantities of xylene and n-butanol at 110°C over a period of 3 hours. The resulting mixture was reacted at the same temperature for 2 hours, giving a resin [H] solution. The resin solution obtained had a solids content of 50%. The resin obtained had a number average molecular weight of 20000, an acid value of 28 mg KOH/resin portion (calculated as solids) (this term indicates the same meaning hereinafter) (corresponding to about 10 carboxyl groups on the average per molecule) and a hydroxyl value of 87 mg KOH/resin portion (calculated as solids) (this term indicates the same meaning hereinafter) (corresponding to about 31 hydroxyl

groups on the average per molecule).

Example 3

5       A 20 parts quantity (calculated as solids) of the foregoing polysiloxane [D] was mixed with 80 parts (calculated as solids) of the above resin [H], giving a composition of Example 3.

Examples 4 to 12

      Compositions of Examples 4 to 12 were prepared using the components shown in Table 2 in the listed amounts.

10       Table 3 shows the properties of the compositions obtained in Examples.

Table 2

Amount (part) (calculated as solids)	Example											
	3	4	5	6	7	8	9	10	11	12		
Polysiloxane [D]	20					20						
Polysiloxane [E]		30					30					
Polysiloxane [F]			30					30				
Polysiloxane [G]				30	30				30	30		
Resin [H]	80	70	70	70		80	70	70	70			
Resin [I]					70					70		
Metal chelate compound						1	1	1	1	1	1	1

Resin [I]: Lumiflon LF-9112 (trade name of a fluorine-containing resin manufactured by Asahi Chemical Industry Co., Ltd.)

Metal chelate compound: Tris(acetylacetonato)aluminum

Table 3

		Example									
		3	4	5	6	7	8	9	10	11	12
Storage stability		1	1	1	1	1	1	1	1	1	1
Appearance and properties	Appearance of film	Sat.	Sat.	Sat.	Sat.	Sat.	Sat.	Sat.	Sat.	Sat.	Sat.
	Gel fraction ratio	90	91	92	93	95	92	93	94	94	98
	Impact resistance	50 <	50 <	50 <	50 <	50 <	50 <	50 <	50 <	50 <	50 <
	Water resistance	Sat.	Sat.	Sat.	Sat.	Sat.	Sat.	Sat.	Sat.	Sat.	Sat.
	Weatherability	Sat.	Sat.	Sat.	Sat.	Sat.	Sat.	Sat.	Sat.	Sat.	Sat.
Acid resistance		1.7	1.2	1.0	1.0	0.8	1.5	1.0	0.8	0.7	0.7

The term "Sat." in Table 3 means "Satisfactory".

The test methods employed in Examples 3 to 12 were as follows.

Storage stability: Each composition adjusted to 1 poise with xylene and n-butanol was placed into a bottle for  
5 containing mayonnaise so that the composition in the bottle was half-full. The composition was allowed to stand at 40°C. for 2 weeks. The variation of the viscosity of the composition was determined and expressed in terms of (viscosity after storage (poise)/viscosity before storage (poise)).

10 Production of films

Each composition was applied to a substrate to a dry film thickness of 30  $\mu$ m and the coated substrate was baked at 120°C for 30 minutes, giving a film.

Appearance of the film: Polished mild steel sheet was used  
15 as a substrate. The substrate was checked for undesirable changes (dulling, shrinkage, cracking, peeling) on the surface thereof.

Gel fraction ratio: The film dried was removed from the glass plate and extracted by Soxhlet extractor at a reflux  
20 temperature for 6 hours using acetone. The remaining portion of the film was expressed in percentages by weight.

Impact resistance: Mild steel sheet was used as a substrate. With use of Du Pont impact tester, a weight of 500 g was dropped on the coated surface and the maximum height  
25 (cm) at which the dropping caused no crack or peeling of the

film was determined.

Water resistance: Mild steel sheet was used as a substrate. The test piece was immersed in warm water (40°C) for 60 days, and the film on the test piece was checked for  
5 undesirable changes.

Weatherability: An aluminum board was used as a substrate. With use of QUV-type weather meter (product of THE Q PANEL Company, ultraviolet light-fluorescent light lamp "No. QFS-40, UV-B", the wavelength was in the range of 320 to 280  
10 nm), the test piece was subjected to a cycle repeatedly for 2000 hours, one cycle consisting of irradiating the test piece (15 minutes) and subjecting the same to condensation (15 minutes) at 40 to 70°C, thereafter the degree of the impairment of the film was observed.

15 Acid resistance: Mild steel sheet was used as a substrate. A 0.4 cc quantity of 40% sulfuric acid was applied dropwise to the film and the applied test piece was dried at 75°C for 15 minutes, followed by washing with water. The depth ( $\mu\text{m}$ ) of the trace (etching) formed by the dropping of sulfuric  
20 acid was measured.

CLAIMS:

1. A curable resin composition comprising (I) at least one polysiloxane resin selected from the group consisting of (i) a polysiloxane resin which is a reaction product prepared by condensation of a silane compound (A) having at least one hydroxyl group and/or hydrolyzable group respectively directly attached to the silicon atom, the polysiloxane resin (i) having at least one hydroxyl group and/or hydrolyzable group respectively directly attached to the silicon atom on the average per molecule of the reaction product, and (ii) a polysiloxane resin which is a reaction product of the silane compound (A) having at least one hydroxyl group and/or hydrolyzable group respectively directly attached to the silicon atom with a silane compound (B) having at least one hydroxyl group and/or hydrolyzable group respectively directly attached to the silicon atom and at least one epoxy group, the polysiloxane resin (ii) having at least one hydroxyl group and/or hydrolyzable group respectively directly attached to the silicone atom on the average, and at least one epoxy group on the average and per molecule of the reaction product, and (II) a hydroxyl-containing resin or a hydroxyl- and carboxyl-containing resin.

2. A curable resin composition according to claim 1 wherein the polysiloxane resin (i) has an average of about

1 to about 50 hydroxyl groups and/or hydrolyzable groups respectively directly attached to the silicon atom, per molecule.

3. A curable resin composition according to claim 1  
5 wherein the polysiloxane resin (ii) is a reaction product prepared by reacting the silane compound (A) and the silane compound (B) in a ratio of between about 10 and about 99.9 mole% of the former and between about 90 and about 0.1 mole% of the latter, based on the combined amount of the two  
10 compounds.

4. A curable resin composition according to claim 1 wherein the polysiloxane resin (ii) has an average of about 1 to about 50 hydroxyl groups and/or hydrolyzable groups respectively directly attached to the silicon atom per  
15 molecule and an average of about 1 to about 50 epoxy groups per molecule.

5. A curable resin composition according to claim 1 wherein the component (I) is the polysiloxane resin (i) and the component (II) is the hydroxyl-containing resin.

20 6. A curable resin composition according to claim 1 wherein the component (I) is the polysiloxane resin (ii) and the component (II) is the hydroxyl- and carboxyl-containing resin.

7. A curable resin composition according to claim 1  
25 wherein the weight ratio of the polysiloxane resin (I) to



the hydroxyl- or hydroxyl- and carboxyl-containing resin (II) is in the range of between about 5/95 and about 95/5.

8. A curable resin composition comprising the curable resin composition as defined in claim 1 and a curing catalyst.

9. A method of curing the curable resin composition as defined in claim 1 or 8, the method comprising the steps of applying the composition to a substrate and curing the coating by heating.